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Characteristics of nonmethane hydrocarbons (NMHCs) in industrial, industrial-urban, and industrial-suburban atmospheres of the Pearl River Delta (PRD) region of south China

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[1] In a study conducted in late summer 2000, a wide range of volatile organic compounds (VOCs) were measured throughout five target cities in the Pearl River Delta (PRD) region of south China. Twenty-eight nonmethane hydrocarbons (NMHCs; 13 saturated, 9 unsaturated, and 6 aromatic) are discussed. The effect of rapid industrialization was studied for three categories of landuse in the PRD: industrial, industrial-urban, and industrial-suburban. The highest VOC mixing ratios were observed in industrial areas. Despite its relatively short atmospheric lifetime (2–3 days), toluene, which is largely emitted from industrial solvent use and vehicular emissions, was the most abundant NMHC quantified. Ethane, ethene, ethyne, propane, *n*-butane, *i*-pentane, benzene, and *m*-xylene were the next most abundant VOCs. Direct emissions from industrial activities were found to greatly impact the air quality in nearby neighborhoods. These emissions lead to large concentration variations for many VOCs in the five PRD study cities. Good correlations between isoprene and several short-lived combustion products were found in industrial areas, suggesting that in addition to biogenic sources, anthropogenic emissions may contribute to urban isoprene levels. This study provides a snapshot of industrial, industrial-urban, and industrial-suburban NMHCs in the five most industrially developed cities of the PRD. Increased impact of industrial activities on PRD air quality due to the rapid spread of industry from urban to suburban and rural areas, and the decrease of farmland, is expected to continue until effective emission standards are implemented.

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1. Introduction

[2] A wide range of volatile organic compounds (VOCs) participate in photochemical reactions in the troposphere, resulting in ozone enhancement and photochemical smog formation. Ozone, a secondary pollutant, has harmful effects on human health and plant growth [e.g. *Burnett et al.*, 1994]. Some VOCs such as 1,3-butadiene and benzene are classified as air toxics, and benzene is a known human carcinogen [*U.S. Environmental Protection Agency* (*USEPA*), 1998]. Recent studies investigating passenger and pedestrian exposure to toxic VOCs in Guangzhou, at the north end of the Pearl River Delta (PRD), found relatively high benzene mixing ratios in public transportation vehicles and along urban roadsides [*Chan et al.*, 2003; *Zhao et al.*, 2004]. Previous work has shown that the predominant anthropogenic sources of VOCs are vehicular and industrial emissions related to fossil fuel combustion, liquefied petroleum gas (LPG) leakage, fuel evaporation, petroleum distillation, and solvent usage [*Cheng et al.*, 1997; *Chen et al.*, 2001; *Na et al.*, 2001; *Seila et al.*, 2001; *Watson et al.*, 2001; *He et al.*, 2002]. The PRD is China's first special economic zone and is characterized with special economic systems and policies that are different from China's typical economic practices. As a result of increasing population and rapid industrialization, the air quality in the PRD region has suffered greatly.

[3] Deteriorating air quality in the PRD is likely related to increasing VOC emissions and has been a cause for concern in recent years. For example, the highest 1-hour O_3 mixing ratio at Chengxi in Foshan (242 ppbv) was recorded in 2000, and the number of hours with visibility impairment (<8 km) increased between 1991 and 2000 in cities throughout the PRD (Shenzhen, Guangzhou, and Hong Kong) [*Hong Kong Environmental Protection Department*

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Figure 1. Map of the Pearl River Delta (PRD) region of Guangdong province, southeast China.

(*HKEPD*), 2002]. The medium and long-range transport of ozone precursors (VOCs, carbon monoxide (CO), and nitrogen oxides (NO_x)) from the PRD can also enhance tropospheric ozone formation, acid precipitation, and the formation of haze in downwind regions. For example, tropospheric ozone peaks are frequently observed during autumn in Hong Kong, when the prevailing north and northeasterly winds bring polluted air from the PRD and ozone is formed during this medium-range transport [*Chan et al.*, 1998]. In addition to appropriate meteorological conditions, local emissions from Hong Kong also contribute to high ozone levels during autumn in the southern China coastal area [*Wang and Kwok*, 2003]. The chemical evolution of Asian continental outflow over the Pacific Ocean during long-range transport to North America has been investigated during comprehensive airborne missions (e.g., the Pacific Exploratory Mission (PEM-West A) of 1991 and the Transport and Chemical Evolution over the Pacific (TRACE-P) mission of 2001). Air pollutants emitted from north Asian countries (e.g., China, Taiwan, and Japan) were characterized [*Talbot et al.*, 1996] and significant levels of photochemical products were found in the continental outflow [e.g. *Jacob et al.*, 2003, and references therein].

[4] Motor vehicles, industry and power plants in the PRD are believed to be the dominant contributors to regional air pollution, commonly seen as haze [*HKEPD*, 2002]. A variety of industries exist in urban, suburban, and rural areas of the PRD. The contribution of VOCs to the ambient atmosphere of the PRD is unknown and was the focus of our study, in particular determining the impact of industrial growth on the region by specifying and quantifying VOCs in industrial, industrial-urban, and industrial-suburban areas of the PRD. Our goal was to achieve a better understanding of the air mass characteristics and source contributions to this rapidly developing region. The data were used to create an initial profile of industrial, industrial-urban, and industrial-suburban NMHCs in the five most industrially developed cities of the PRD. In addition, the sampling of VOCs from various high-impact industrial emission sources provides a benchmark for the selection of industries for further intensive study.

2. Experiment

2.1. Sampling Design

[5] The PRD region is situated within Guangdong province in the southeast corner of China and is composed of nine smaller cities (Figure 1). Each smaller city consists of a densely populated and developed central city surrounded by its perimeter county-level cities, districts, and towns. For example, Guangzhou is the center city of the Guangzhou city, whose area covers other relatively less developed perimeter county-level cities and districts such as Huadu, Conghua, Zengcheng, and Panyu, to form the greater Guangzhou city. The total area of the PRD is about 42,000 km^2. Because of the lack of landuse planning and control in the past, industrial activities, including heavy polluting ones, are everywhere. Rapid industrialization leads to the spread of industrial activities from urban to suburban areas and even to rural areas. For example, at present there are more than 18,000 industrial organizations and approximately 20,000 small-sized village, and privately, owned factories and mills within the heavily industrialized Dongguan city. This is about 15 times more than were present in 1980.

[6] In order to understand the VOC profile and evaluate the impact of industrialization on air quality in the PRD, the five most industrially developed cities were targeted for sampling. Seventy-eight ambient air samples were collected throughout Dongguan, Foshan, Guangzhou, Jiangmen, and Zhongshan, focusing on three categories of sampling environment: industrial, industrial-urban, and industrial-suburban, henceforth referred to as T1, T2, and T3, respectively (Table 1). The number of samples collected in each city was determined according to their industrial activities and their significance to the PRD industrial production output. Dongguan, Foshan, and Guangzhou are more industrially developed than Jiangmen and Zhongshan, and therefore a greater number of samples were collected there. Over 40% of the air samples were collected in Dongguan, while about 20% of the samples were collected in each of Foshan and Guangzhou. The sampling locations were selected to study the characteristic industrial VOC emissions and the effect of these emissions on densely populated neighborhoods. Al-

Table 1. Sample Collection Details Throughout Five Cities of the Pearl River Delta Based on Three Categories of Sampling Environments[a]

	Sample Collection			
Cities	Type 1 (T1)	Type 2 (T2)	Type 3 (T3)	Total
Dongguan	5	7	20	32
Foshan	3	7	5	15
Guangzhou	7	5	5	17
Jiangmen	0	3	4	7
Zhongshan	0	3	4	7
Total	15	25	38	78

[a]T1: Sampling near a significant industrial point source or an industrial complex (industrial); T2: sampling in an area (away any known point sources) with mixed industrial and urban sources (industrial-urban); T3: sampling in an area (away any known point sources) with mixed industrial and suburban/rural sources (industrial-suburban).

Table 2. Mean Mixing Ratios of Measured Volatile Organic Compounds[a]

	T1 (n = 15)	T2 (n = 25)	T3 (n = 38)
CH_4, ppmv	2.1 ± 0.1[b]	2.0 ± 0.1	2.0 ± 0.1
CO, ppmv	1.4 ± 2.4	0.7 ± 0.6	0.5 ± 0.2
Ethane	2.3 ± 1.3	1.8 ± 0.6	1.4 ± 0.6
Propane	3.7 ± 2.5	2.5 ± 1.4	2.1 ± 1.7
n-Butane	2.6 ± 1.7	1.5 ± 0.9	1.3 ± 1.0
i-Butane	1.6 ± 0.8	1.0 ± 0.5	0.8 ± 0.6
n-Pentane	1.3 ± 2.3	0.5 ± 0.4	0.4 ± 0.2
i-Pentane	2.2 ± 1.5	1.3 ± 0.7	0.9 ± 0.4
2-Methylpentane	1.0 ± 1.1	0.5 ± 0.3	0.5 ± 0.7
3-Methylpentane	0.6 ± 0.6	0.3 ± 0.2	0.4 ± 0.6
n-Hexane	1.1 ± 2.1	0.4 ± 0.2	0.5 ± 0.9
2-Methylhexane	1.1 ± 1.5	0.6 ± 0.7	0.5 ± 0.4
3-Methylhexane	0.9 ± 1.1	0.5 ± 0.5	0.4 ± 0.3
2,3-Dimethylpentane	0.3 ± 0.4	0.2 ± 0.2	0.1 ± 0.1
n-Heptane	1.4 ± 2.3	0.4 ± 0.6	0.4 ± 0.3
Ethene	5.1 ± 3.8	2.6 ± 1.3	2.0 ± 1.1
Ethyne	6.0 ± 3.0	4.0 ± 1.5	3.1 ± 1.7
Propene	1.1 ± 0.8	0.6 ± 0.3	0.4 ± 0.2
trans-2-Butene	0.3 ± 0.3	0.2 ± 0.1	0.1 ± 0.1
cis-2-Butene	0.3 ± 0.2	0.1 ± 0.1	0.1 ± 0.1
1-Butene	0.4 ± 0.3	0.2 ± 0.1	0.1 ± 0.1
i-Butene	0.4 ± 0.3	0.3 ± 0.1	0.2 ± 0.2
1,3-Butadiene	0.2 ± 0.1	0.1 ± 0.2	0.1 ± 0.1
Isoprene	0.6 ± 0.3	0.4 ± 0.2	0.5 ± 0.7
Benzene	2.8 ± 1.7	2.0 ± 1.1	1.3 ± 0.8
Toluene	13.5 ± 11.8	11.5 ± 11.6[c]	7.3 ± 5.4
Ethylbenzene	2.0 ± 3.5	0.9 ± 1.0	0.8 ± 0.7
o-Xylene	1.2 ± 1.4	0.7 ± 1.0	0.5 ± 0.5
m-Xylene	3.6 ± 7.1	1.6 ± 2.2	1.1 ± 1.2
p-Xylene	1.3 ± 1.8	0.9 ± 1.6	0.6 ± 0.6
Total NMHCs[d]	62.5 ± 40.2	40.2 ± 21.2	31.2 ± 13.8

[a]Mean mixing ratios in ppbv, unless otherwise specified.
[b]Mean ± standard deviation.
[c]Owing to its exceptionally high value (77 ppbv), one value was excluded in the calculation of the mean toluene mixing ratio.
[d]That is, CH_4 and CO are excluded.

though the impact of the phenomenal increase of motor vehicles in the PRD on atmospheric VOCs is an important concern [*Guangzhou Yearbook Editorial Committee* (*GZYEC*), 2000], it was not the focus of our study. As such, urban city/town centers with heavy traffic, commercial areas and residential areas with little industrial activities were not studied, with the exception of two roadside samples collected in high density traffic in urban Guangzhou to illustrate the profile of vehicular VOC emissions in the PRD.

[7] The sampling design enabled the collection of air characteristic of industrial emissions and the study of the regional impact of these emissions. The three categories of air samples are as follows: T1 samples were collected next to either an industrial point source or a cluster of industries. These included facilities associated with paper production, shoemaking, cement and ceramic manufacture, and food processing, and a steel plant and a petrochemical plant. The facilities were usually 2–3 stories high. Steel plants and cement factories consume large amounts of fuel, while the shoemaking industry involves heavy solvent usage. The T1 samplings were focused in Dongguan, Foshan, and Guangzhou, where a wide variety of industries are distributed. VOC profiles for different industries were also obtained.

[8] The T2 samples were collected in all five cities and measured the ambient air in town/city sectors with active industrial activities. The sampling sites were selected such that they were not under the direct influence from any point sources, giving a sample with an integrated VOC composition typical of ambient urban air. For instance, the rooftops of government buildings and primary schools were typically selected. Industrial emissions, in addition to those from vehicles, were expected to contribute to the VOC loading.

[9] Similarly, T3 samples were collected at selected rooftop sites and away from any known point sources. These sampling sites were located in suburban and rural areas that had some industrial activities. These sites experienced less influence from vehicular emissions than the T1 or T2 sites, while the recent spread of industry into suburban and rural areas increased the impact of industrial VOC emissions at the T3 sites.

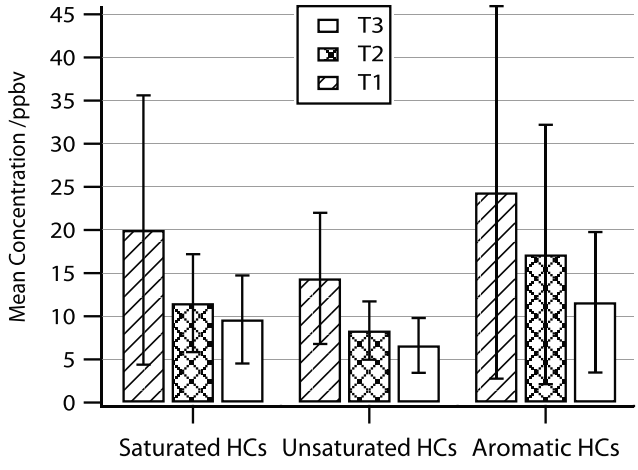

Figure 2. Average mixing ratios of three NMHC groups for the three categories of sampling environment.

2.2. Sample Collection and Analysis

[10] Between 11 August and 19 September 2000, a total of 78 ambient air samples and two roadside samples were collected using evacuated 2L stainless steel canisters (each equipped with a bellows valve) throughout the five PRD target cities. Thirty-two air samples were collected in Dongguan on 11 and 12 August, and the remaining samples were collected in the other four cities between 7 and 19 September. All samples were collected between 0900 and 1700 local time, when factories were under normal operation.

Table 3. Mean Mixing Ratios, ppbv, of the 10 Most Abundant NMHCs in the Three Study Areas (Standard Deviations Are Listed in Table 1)

	T1	Mean	T2	Mean	T3	Mean
1	Toluene	13.5	Toluene	11.5	Toluene	7.3
2	Ethyne	6.0	Ethyne	4.0	Ethyne	3.1
3	Ethene	5.1	Ethene	2.6	Propane	2.1
4	Propane	3.7	Propane	2.5	Ethene	2.0
5	*m*-Xylene	3.6	Benzene	2.0	Ethane	1.4
6	Benzene	2.8	Ethane	1.8	Benzene	1.3
7	*n*-Butane	2.6	*m*-Xylene	1.6	*n*-Butane	1.3
8	Ethane	2.3	*n*-Butane	1.5	*m*-Xylene	1.1
9	*i*-Pentane	2.2	*i*-Pentane	1.3	*i*-Pentane	0.9
10	Ethylbenzene	2.0	*i*-Butane	1.0	Ethylbenzene	0.8

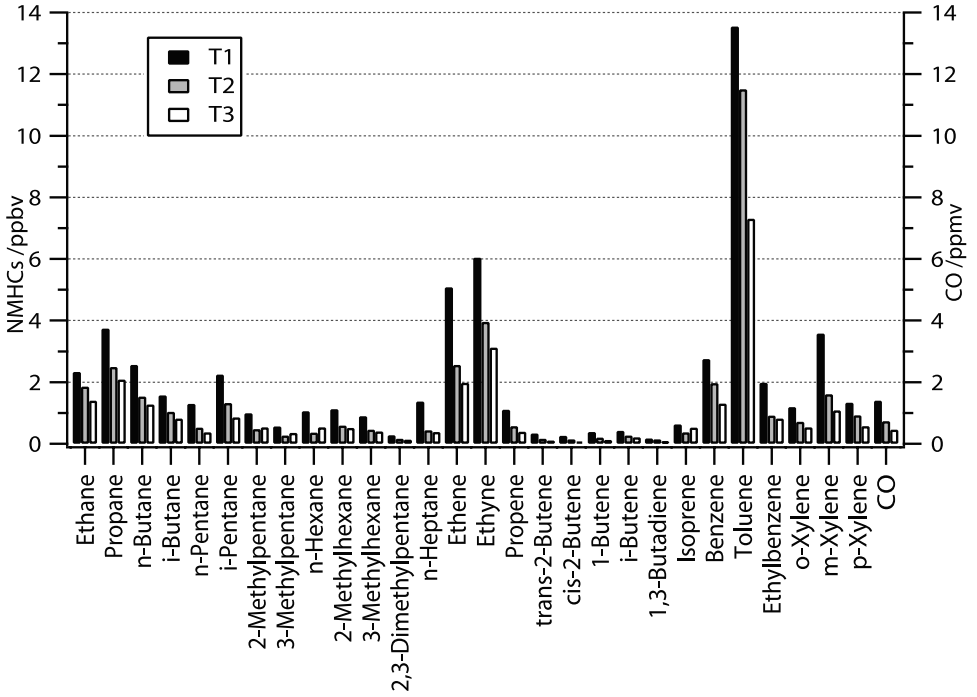

Figure 3. Average mixing ratios of NMHCs (ppbv) and CO (ppmv) for the three landuse categories.

[11] Prior to sampling, the canisters were conditioned and evacuated by University of California, Irvine (UCI) group members, using procedures described by *Blake et al.* [1994]. Air sampling was performed by partially opening the canister valve and collecting air for about one minute in order to obtain "integrated" air samples. After sampling, all canisters were shipped to the UCI laboratory and analyzed for 60 compounds, including CO, methane (CH_4), NMHCs, halocarbons, and alkyl nitrates. Of these compounds, CO, CH_4, and 28 NMHCs (of which 13 are saturated, 9 are

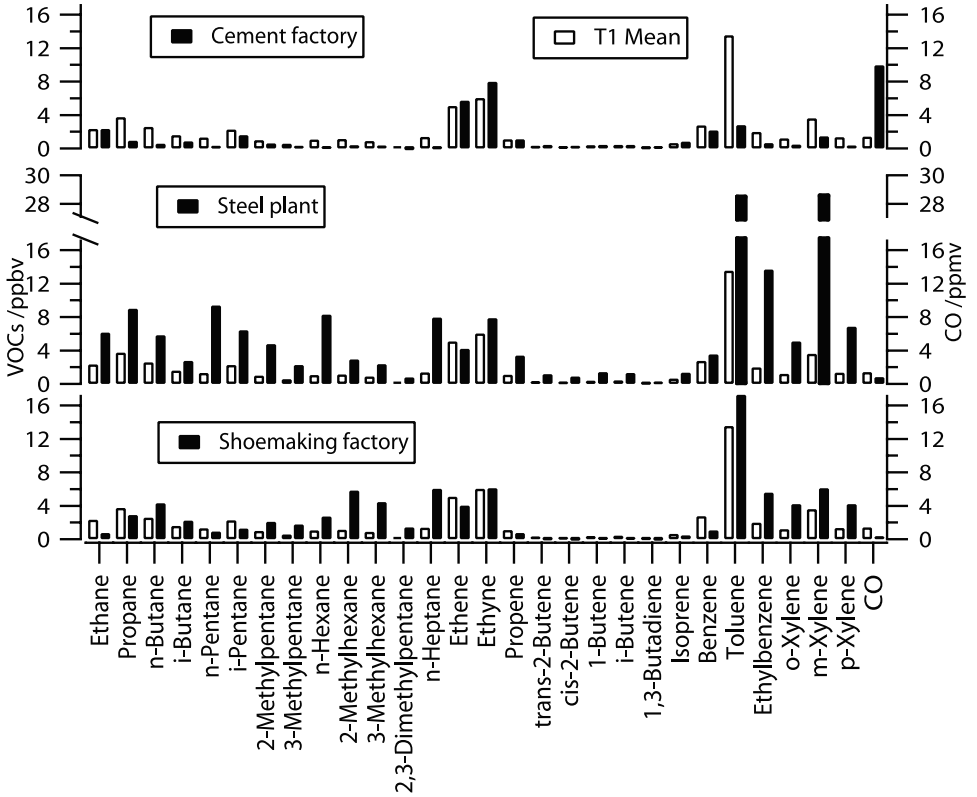

Figure 4. NMHC mixing ratios for three important types of industrial samples collected in T1.

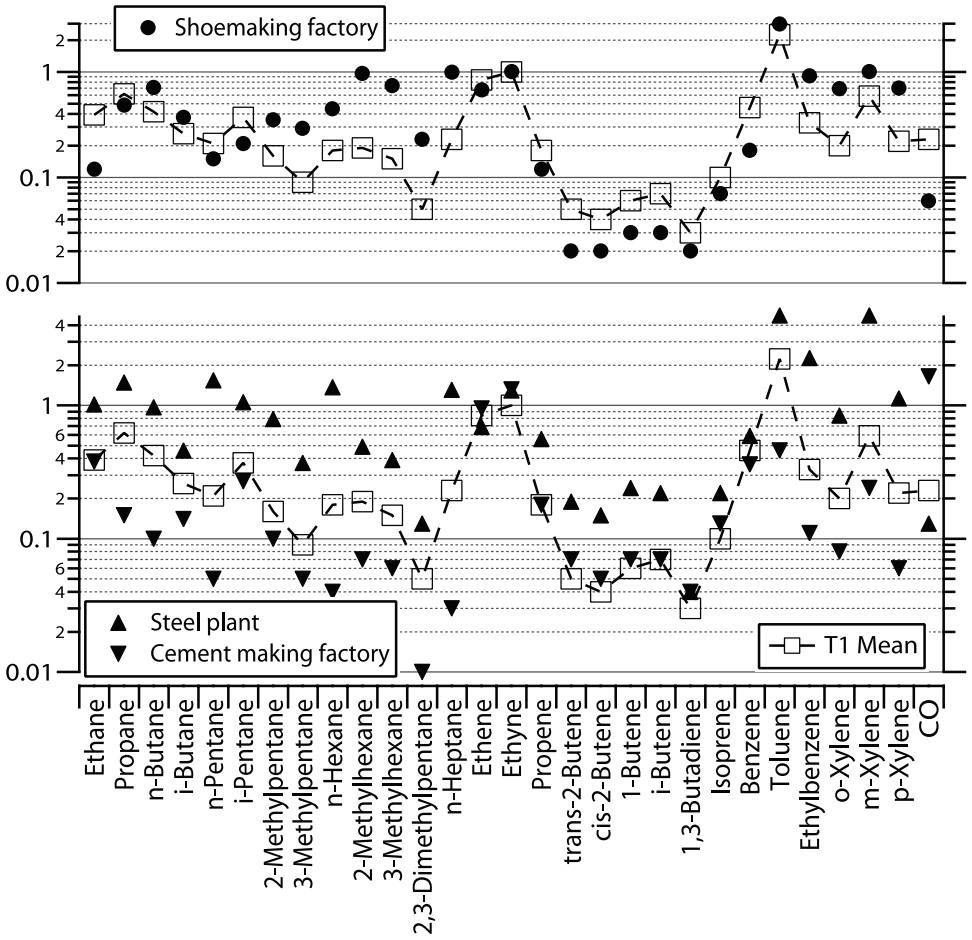

Figure 5. NMHC fingerprints (normalized to ethyne) for three important types of industrial samples collected in T1.

unsaturated and 6 are aromatic; see Table 2) are discussed here. Details of the analytical system, data analysis, and quality control procedures are described by *Colman et al.* [2001] and *Barletta et al.* [2002].

3. Results and Discussion

3.1. General NMHC Characteristics

[12] Average mixing ratios and standard derivations were determined for the three sampling environments for CH_4, CO, and the 28 NMHCs (Table 2). There was one exceptionally high toluene value in the industrial-urban category (77 ppbv), which was removed in the overall statistical analysis because it was clearly influenced by a nearby and unknown source.

[13] The average mixing ratios of the saturated, unsaturated, and aromatic hydrocarbons are given for each category in Figure 2. The unsaturated hydrocarbons (ethene, ethyne, and propene) were found to be the dominant component in vehicular exhaust on roadsides in the PRD (section 3.3), similar to other urban areas [*Derwent et al.*, 1995; *McLaren et al.*, 1996; *Watson et al.*, 2001]. The lowest mean ratio of saturated hydrocarbons to unsaturated hydrocarbons (1.4) was observed in T2. This is consistent with greater vehicular emissions in the more developed urban areas as opposed to a larger contribution from fresh industrial emissions in T1, and a smaller vehicle density in T3. Additionally, alkane mixing ratios were elevated in T1 compared to T2 and T3, most likely as a result of solvent use or by-product emissions and vaporization from poorly controlled industrial facilities.

[14] The ten most abundant NMHC gases from this study are tabulated in Table 3. Toluene was the most abundant gas in all three categories of landuse and its mean was higher than the second most abundant species, though we note the high standard deviations associated with these means (see Table 2). Vehicular emissions frequently contribute to high toluene levels on Guangzhou roadsides [*Zhao et al.*, 2004], and toluene is also the major component of many industrial solvents and paints in the PRD [*He et al.*, 2002], as in other countries [*Sweet and Vermette*, 1992; *Seila et al.*, 2001]. Printing, shoemaking, toy manufacturing, and electronic industries use large amounts of solvents and paints [*He et al.*, 2002], and these industries likely accounted for the high abundances of toluene and *m*-xylene, particularly in T1. High levels of ethane, ethene, ethyne, propane, *i*-pentane, *n*-butane, benzene, and *m*-xylene were also observed in all three categories and were likely associated with fuel combustion emissions, gasoline evaporation, LPG leakage and solvent usage [*Chen et al.*, 2001; *Kang et al.*, 2001; *Watson et al.*, 2001; *Borbon et al.*, 2002].

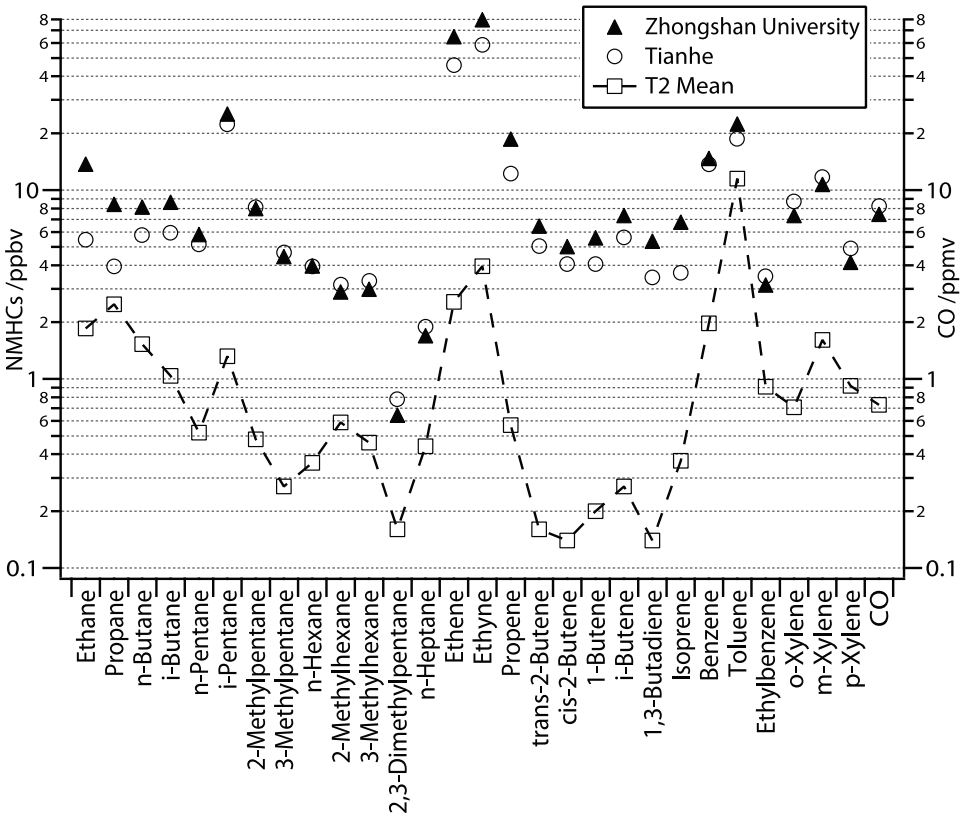

Figure 6. NMHC and CO mixing ratios from two vehicular source samples in urban roadside (Guangzhou).

3.2. Impact of Industrial Emissions

[15] The average mixing ratios of NMHCs (ppbv) and CO (ppmv) measured in the three categories are shown in Figure 3. Their average mixing ratios generally followed the trend T1 > T2 > T3, showing that fresh industrial emissions made significant contributions to the NMHC and CO mixing ratios. The standard deviations were very large in each category (Table 2), especially in T1 due to differences in emission strengths from industrial sources. We selected three serious polluting industries with characteristic VOC emissions for discussion, specifically cement making factories, shoemaking factories, and a steel plant. These industries were found to greatly contribute to the ambient mixing ratios of several species in the nearby atmosphere (Figure 4). The cement making factories emitted large amounts of CO compared to the T1 mean, while the shoemaking factories and the steel plant emitted large amounts of aromatics and alkanes.

[16] To further examine the short-lifetime alkenes and to evaluate the contribution of combustion to ambient VOC levels, we normalized the gases to the mean T1 ethyne mixing ratio (6.0 ± 3.0 ppbv), as shown in Figure 5. Ethyne is a relatively photochemically stable compound in the atmosphere. Ethyne is a general tracer of incomplete combustion, and fuel combustion in vehicles and industrial boilers are included among its sources. Bearing in mind the large standard deviation associated with the mean T1 ethyne value and the single sample (with no accompanying statistics) for each of the three industries, ethyne's T1 mixing ratio (6.0 ppbv) is similar to that of the shoemaking sample (6.1 ppbv). Larger ethyne mixing ratios found in the steelmaking sample (7.9 ppbv) and cement-making sample (8.0 ppbv), which suggests the importance of fuel combustion from certain industrial sources.

[17] Shoemaking is a major industry in Dongguan, with factories widely spread throughout the city. It is a common practice to immerse shoemaking materials in solvents overnight to enhance their oil-resisting property. These VOCs can easily escape into the ambient air when the solvent evaporates. Toluene and *n*-hexane are major components in various solvents, which are commonly used in shoemaking industries and in other industries involving furniture, toy, and leather manufacturing, and printing and electronic production [*He et al.*, 2002]. *n*-Hexane and to a lesser extent toluene were enhanced in the sample collected outside shoemaking factories as compared to the T1 average, as were seven C_6–C_7 alkanes and five aromatics.

[18] Cement industries are concentrated in Zengcheng in the Guangzhou city. Heavy fuel consumption likely led to the highest measured mixing ratio of ethyne in Zengcheng. Although benzene and some alkenes were enhanced compared to the T1 mean, CO showed the most noticeable deviation from the T1 mean, and extremely high CO mixing ratios measured outside many cement factories were associated with heavy fuel combustion and poor ventilation systems.

[19] One sample collected outside a large steel plant in the urban area of Guangzhou showed significant increases in almost all NMHC mixing ratios (Figure 5), compared to the normalized T1 means and the cement making sample.

Table 4. Mean Ratio of Toluene to Benzene for the Three Different Landuse Categories (T1, T2, and T3) and for the Roadside Samples

Toluene/Benzene (T/B)		
Types	Mean ± S.D.	Range
T1	6.3 ± 8.0	1.3–32.0
T2	6.0 ± 4.7	1.1–19.2
T3	6.9 ± 5.6	1.1–26.5
Roadside	1.4 ± 0.1	1.4–1.5

This suggests that additional sources of NMHCs other than fuel combustion were present. Leakage of coke gas from the heating and cooling cycles in the plants' coke ovens and fugitive emissions from metal surface cleaning were likely additional NMHC contributors. Carbon monoxide levels were comparable to the T1 mean because there is sufficient oxygen input to the basic oxygen furnace, which led to relatively complete combustion at high temperature [*USEPA*, 1995]. Hence the production of CO via incomplete combustion was greatly reduced in the steel industry relative to the cement industry, which requires lower oven temperatures for cement production.

[20] In summary, in the proximity of major industrial activities, direct emissions contribute highly to the neighboring atmosphere. This led to spatial variations of the VOC profile in the five PRD cities and high concentration variability for several VOC species. Because one sample from each industry is not enough to accurately determine their contributions to the local atmosphere, more samples should be collected in future studies.

3.3. Impact of Vehicular Emissions

[21] It is difficult to separate industrial and vehicular contributions to VOC mixing ratios in the industrial-urban atmosphere. Hence we collected two urban roadside samples to specifically examine the impact of vehicular emissions. Figure 6 shows the NMHC and CO mixing ratios from the two samples together with the mean T2 mixing ratios. At the roadside sites the mean mixing ratios for all NMHCs (saturated, unsaturated and aromatic) were much higher than the mean levels in T2. Several important vehicular emission markers such as ethane, ethyne, propene, and *i*-pentane exhibited substantially higher mixing ratios in the roadside samples.

[22] In the five PRD cities, motorcycles are very popular due to their low cost and mobility. Motorcycles dominate the distribution of motor vehicles, with about 75% of all motor vehicles being motorcycles in 2000. In addition to their great abundance, poor maintenance and poor emission controls on motorcycles lead to high VOC emissions that negatively impact ambient air quality. *Tsai et al.* [2003] investigated the emissions of VOCs from motorcycle engine exhaust at different driving modes and found that *i*-pentane, toluene, 2-methylpentane, 3-methylpentane, *n*-pentane, and benzene were frequently emitted from exhaust gas of motorcycles under all driving conditions. With the exception of toluene, which showed a smaller relative enhancement, these motorcycle exhaust-related VOCs were strongly elevated in our two roadside samples.

[23] The mean ratios of toluene to benzene (T/B) in the three sampling environments and for the roadside samples are tabulated in Table 4. Bearing in mind the large standard deviation associated with the T2 mean, the mean T/B ratio at T2 (6.0 ± 4.7) was about 4 times larger than that for the roadside sample (1.4 ± 0.1). The T3 site (T/B ratio of 6.9 ± 5.6) may be less influenced by vehicular exhaust than the T1 and T2 sites, though the large standard deviations associated with the T1, T2, and T3 averages do not allow a clear conclusion. The large T/B ratios at T1, T2, and T3 compared to the roadside samples indicate that there were significant industrial toluene emissions at all three sites, which outweighed the faster photochemical loss of toluene relative to benzene. Unlike T1, which was affected by clustered point sources, some T2 and T3 rooftop samples were influenced by scattered industries using heavy toluene-containing solvents.

[24] The roadside T/B ratio (1.4 ± 0.1) was within the range obtained in three PRD cities (1.16–2.23) [*Wang et al.*, 2002] and was similar to that observed in Birmingham, UK (1.85) [*Kim et al.*, 2001]. Smaller T/B ratios (1.16–1.24) were obtained inside a tunnel in Guangzhou, and higher ratios were obtained from roadside samples in Macau and Nanhai (1.57–2.23) [*Wang et al.*, 2002]. The smaller roadside ratio from our study may be due to differences in fuel composition, the extent of background dilution, and individual photochemical reactivity. Higher T/B ratios have been found in urban air in other countries, such as 2.38 in Rome [*Brocco et al.*, 1997] and 1.43 to 2.58 in four Latin American cities [*Gee and Sollars*, 1998]. Significantly higher T/B ratios were obtained in two other Asian cities, Bangkok and Manila (8.66 and 11.30, respectively) [*Gee and Sollars*, 1998] and downwind of a Nylon-dyeing plant in Taiwan (14.19) [*Lin*, 2001], indicating that additional sources of toluene from industrial activities can drastically increase the T/B ratio.

[25] We further note that propane was elevated in the roadside samples compared to the T2 mean (Figure 6). In the PRD, the number of LPG-fuelled vehicles was small in 2000. Thus the observed propane enhancements in the roadside samples were not driven by LPG leakage in automobiles. Instead, we attribute the enhanced propane levels to leakage of natural gas and LPG from refuelling centers and domestic usage. In the PRD, total LPG sales were 3.5×10^6 tonnes in 2000 [*Tian*, 2002] and LPG was mainly used for heating and cooking.

3.4. Anthropogenic Hexane and Isoprene

[26] The *n*-hexane levels were the highest in T1 (Table 2). Hexane is a common component in architectural coatings-

Table 5. Linear Correlations, r^2, Between Isoprene and Other Quantified VOC Combustion Products

	Ethene	Ethyne	Propene	*trans*-2-Butene	*cis*-2-Butene	1-Butene	*i*-Butene	1,3-Butadiene	Benzene
T1	0.01	0.07	0.41	0.55	0.53	0.51	0.49	0.20	0.05
T2	0.00	0.00	0.01	0.14	0.18	0.03	0.06	0.03	0.00
T3	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00

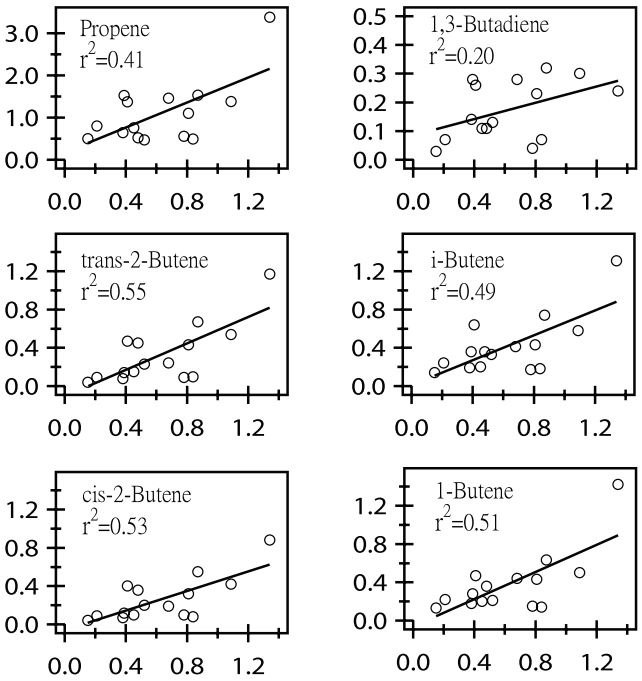

Figure 7. Correlation between isoprene and six combustion products for the T1 landuse category (mixing ratios in ppbv).

composite solvents [*Kang et al.*, 2001] and paint thinners. We suggest that solvent emission from industrial usage contributed to the high *n*-hexane concentrations in T1. The comparable *n*-hexane levels in T2 and T3 (rather than lower levels in T3) is likely explained by rapid industrialization and economic growth in recent years in suburban and rural areas where land is cheaper and readily available. The amount of new housing areas and factories in T3 increased rapidly during the late 1990s and early 2000s, and there were likely considerable emissions from surface coating solvents used in T3 construction that contributed to the enhanced *n*-hexane levels.

[27] In previous reports, isoprene was a dominant biogenic hydrocarbon observed in rural areas [*Jobson et al.*, 1994; *Riemer et al.*, 1998]. However, isoprene has also been identified as a product of vehicular fuel combustion [*Barletta et al.*, 2002]. In addition, good correlation between isoprene and 1,3-butadiene was reported by *McLaren et al.* [1996], especially when air samples were collected next to a roadside. In our study the linear correlation between isoprene and 1,3-butadiene was poor (<0.2) and indicated that isoprene's major source was not vehicular exhaust (Table 5). However, isoprene in T1 had much better correlations with five other combustion products (propene, *trans*-2-butene, *cis*-2-butene, 1-butene, and *i*-butene) than in T2 and T3, which were not significant (Figure 7). The fair correlations between isoprene and five short-lived unsaturated hydrocarbons in T1 indicate they were emitted from local sources. This suggests a shift in the major sources of isoprene from biogenic and combustion (T1) to biogenic emissions (T3). In T3 it is anticipated that the contribution of isoprene from combustion sources will increase and the contribution from biogenic sources will decrease in the coming years, in part because the farmland near T3 is being used more and more for factories and housing estates.

4. Conclusions

[28] A total of 78 ambient air samples were collected throughout five target cities in the PRD that were known to have high industrial activities. Higher VOC mixing ratios were generally measured in industrial areas, followed by industrial-urban areas and industrial-suburban areas. High industrial solvent usage contributed to very high toluene mixing ratios. Apart from solvent emissions, elevated mixing ratios of toluene and the next eight most abundant VOC species can be attributed to fuel combustion from industries and automobiles, and LPG leakage. In the proximity of industrial activity, direct emissions were found to contribute highly to the ambient air VOC loading. Correlations between isoprene and five short-lived unsaturated hydrocarbons that are associated with combustion suggest that industrial boilers were a significant source of isoprene in T1 industrial areas.

[29] Our study provides an initial snapshot of industrial, industrial-urban, and industrial suburban NMHCs in the five most industrially developed cities of the PRD. This preliminary study demonstrates that industrial emissions contribute significantly to the VOC composition of ambient air in the PRD. Variations in (1) the density of industries in the five target cities and (2) direct emissions from different major industries were the likely cause of the spatial variation of the VOC profiles and concentrations in the five PRD areas. More importantly, the trend of increasing industrialization from urban to suburban and rural areas suggests that the entire PRD region will become more and more influenced by industrial pollution in the coming decades. We recommend a full scale study with greater sampling size, more point source characterization, and rigorous landuse sampling. The suggested study is necessary in order for the proper implementation of emission regulations that will begin the reversal of the current trend of increasing ozone concentrations and the number of hazy days.

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